Residual and Contact Herbicide Transport through Field Lysimeters via Preferential Flow

R. W. Malone,* M. J. Shipitalo, R. D. Wauchope, and H. Sumner

ABSTRACT

Usage of glyphosate [*N*-(phosphonomethyl)-glycine] and glufosinate [2-amino-4-(hydroxy-methylphosphinyl)butanoic acid] may reduce the environmental impact of agriculture because they are more strongly sorbed to soil and may be less toxic than many of the residual herbicides they replace. Preferential flow complicates the picture, because due to this process, even strongly sorbed chemicals can move quickly to ground water. Therefore, four monolith lysimeters (8.1 m² by 2.4 m deep) were used to investigate leaching of contact and residual herbicides under a worst-case scenario. Glufosinate, atrazine (6-chloro-*N*²-ethyl-*N*⁴-isopropyl-1,3,5-triazine-2,4-diamine), alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl) acetamide], and linuron (3-3,4-dichlorophenyl-1-methoxy-1-methylurea) were applied in 1999 before corn (*Zea mays* L.) planting and glyphosate, alachlor, and metribuzin [4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4*H*)-one] were applied in 2000 before soybean [*Glycine max* (L.) Merr.] planting. A high-intensity rainfall was applied shortly after herbicide application both years. Most alachlor, metribuzin, atrazine, and linuron losses occurred within 1.1 d of rainfall initiation and the peak concentration of the herbicides coincided (within 0.1 d of rainfall initiation in 2000). More of the applied metribuzin leached compared with alachlor during the first 1.1 d after rainfall initiation (2.2% vs. 0.035%, $P < 0.05$). In 1999, 10 of 24 discrete samples contained atrazine above the maximum contaminant level (atrazine maximum contaminant level [MCL] = 3 µg L⁻¹) while only one discrete sample contained glufosinate (19 µg L⁻¹, estimated MCL = 150 µg L⁻¹). The results indicate that because of preferential flow, the breakthrough time of herbicides was independent of their sorptive properties but the transport amount was dependent on the herbicide properties. Even with preferential flow, glyphosate and glufosinate were not transported to 2.4 m at concentrations approaching environmental concern.

Farm management decisions should include consideration of economics and environmental protection. Negative environmental impacts include pesticide leaching into ground water or subsurface drains above acceptable levels. Alachlor and atrazine are often detected in runoff and ground water, and concentrations frequently exceed the MCL (e.g., Shipitalo et al., 1997; Kolpin et al., 1998; Wade et al., 1998). The MCL is an enforceable standard

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that takes into consideration cost (treatment technology, limits of detection) and the maximum level of a contaminant in drinking water at which no known or anticipated adverse effect on the health of persons would occur with an adequate margin of safety. The concern of herbicide concentrations exceeding the MCL may be reduced by replacing residual corn and soybean herbicides (alachlor, metribuzin, atrazine) with contact herbicides like glyphosate and glufosinate. Based on PRZM–EXAMS model simulations, Wauchope et al. (2002) concluded that because of their lower application rates and greater soil sorptivity, glyphosate and glufosinate loads in surface runoff should be one-fifth to one-tenth those of atrazine and alachlor. Also, given the significantly lower chronic mammalian toxicity of these compounds, and their vulnerability to breakdown in the drinking water treatment process, risk to human populations may be reduced (Wauchope et al., 2002).

The introduction of transgenic, glyphosate- and glufosinate-tolerant crops has resulted in commonplace glyphosate usage and is expected to result in increased usage of glufosinate (Allen-King et al., 1995). In the United States in 2002, 28.7 Gg of glyphosate was applied to corn (0.8 kg ha⁻¹ yr⁻¹) and soybean (1.2 kg ha⁻¹ yr⁻¹) and 0.3 Gg of glufosinate (0.4 kg ha⁻¹ yr⁻¹) was applied to corn (USDA National Agricultural Statistics Service, 2003). In the same year, 16.2 Gg of atrazine was applied to corn (1.3 kg ha⁻¹ yr⁻¹) and 0.9 Gg of alachlor was applied to corn (2.4 kg ha⁻¹ yr⁻¹) and soybean (1.4 kg ha⁻¹ yr⁻¹) (USDA National Agricultural Statistics Service, 2003). Despite the now commonplace use of contact herbicides on transgenic crops, published field leaching studies of glyphosate and glufosinate are almost nonexistent.

One reason more leaching studies have not been conducted is that the risk is generally regarded to be low. A lysimeter study with undisturbed soil (0.5 m² by 1.1 m deep) found mean yearly glyphosate concentrations below 0.1 µg L⁻¹, but no clear macropore flow was observed (Fomsgaard et al., 2003a, 2003b). Also, Faber et al. (1997) concluded that glufosinate did not leach below 100 mm in soil, but their experiment was not designed to investigate preferential flow and conclusions were mostly based on soil samples from a high organic matter forest soil. Malone et al. (2000b) concluded that soil samples may not adequately quantify herbicide transport when preferential flow occurs. Glyphosate, however, has been detected in well water (Smith et al., 1996) and laboratory studies suggest that glufosinate will move unretarded in sandy aquifers (Allen-King et al., 1995). Moreover, de Jonge et al. (2000) detected glyphosate concentrations in percolate approaching 700 µg L⁻¹

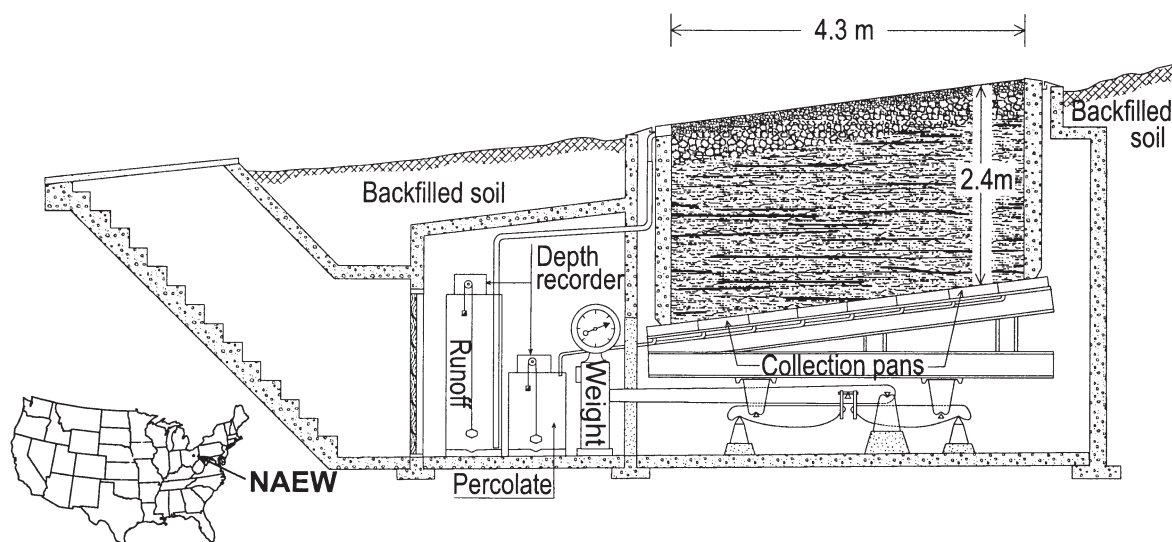**Abbreviations:** MCL, maximum contaminant level.

Fig. 1. Schematic and location of the Coshocton weighing lysimeters (not drawn to scale).

when applied glyphosate was transported through 200-mm-deep undisturbed soil columns with natural macropores. Although de Jonge et al. (2000) studied only the top 200 mm of soil, the surface soil may sorb the majority of chemicals, and water and chemical flow through soil may be more preferential as water and chemicals move deeper into the profile (Kung, 1990a, 1990b; Ghodrati and Jury, 1990). Because the field leaching characteristics of glufosinate and glyphosate are uncertain and because these contact herbicides are now widely used, more investigation is necessary.

Preferential flow occurs when water and chemicals move through a small portion of the soil volume. As water moves through a smaller percentage of the soil, flow becomes more rapid and the soil volume available for chemical sorption decreases. Preferential flow causes pesticides to leach more rapidly and to move more deeply than expected given their chemical properties (K_{oc}, sorption to soil), increasing the potential for ground water contamination. Numerous studies have investigated preferential flow, but Flury (1996) concluded that studies with pesticides of different soil sorption characteristics applied simultaneously in the field are needed. A few studies suggest that herbicides with different sorption characteristics may have similar travel times and leach to similar depths, but mass leached is dependent on sorption to soil (Kladivko et al., 1991; Flury et al., 1995; Traub-Eberhard et al., 1995; Elliott et al., 2000; Jaynes et al., 2001). No studies, however, are available that directly investigate the leaching of alachlor, atrazine, metribuzin, linuron, glufosinate, and glyphosate in the field under a worst-case scenario.

Therefore, our objectives were to (i) investigate the leaching of contact and residual herbicides under a worst-case scenario (heavy simulated rainfall shortly after herbicide application under conditions of preferential flow) and (ii) investigate the preferential flow characteristics of herbicides with different soil sorption. For this purpose, monolith lysimeters were used because they provide a well-defined boundary with one-dimen-

sional vertical flow and allow accurate determination of transport (product of pesticide concentration and water volume).

MATERIALS AND METHODS

Lysimeter Characteristics

Field studies were conducted using one of three sets of monolith (undisturbed soil-block type) lysimeters maintained by the USDA-ARS at the North Appalachian Experimental Watershed near Coshocton, OH (Fig. 1 and 2). The four lysimeters (called Y103A, B, C, and D) have a 6% slope, were constructed between 1937 and 1940, are 8.1 m^2 in surface area, 2.4 m deep, and have four steel side wall strips that protrude approximately 40 mm into the soil monolith to reduce side wall leakage. Recent nitrate leaching studies did not detect side wall leakage with these lysimeters (Owens et al., 1995, 2000). The soil is a Keene silt loam (fine-silty, mixed, mesic Aquic Hapludalfs), which was in chisel till with a corn–soybean rotation beginning in 1985. The most recent soil organic carbon measurements from an adjacent watershed with similar soil and management were 15 g kg^{-1} (0–25 mm), 13 g kg^{-1} (25–75 mm), and 11 g kg^{-1} (75–150 mm). Clay, silt, pH, and bulk density measurements to 1.3 m from Kelley et al. (1975) are presented (Table 1); recent surface bulk density measurements are similar to the 0- to 0.23-m measurements in Table 1. The bottom of the lysimeter extends into fractured shale where steel pans collect percolate that is directed to a collection tank. Percolation rate and quantity are determined every five minutes using a float system connected to a potentiometer
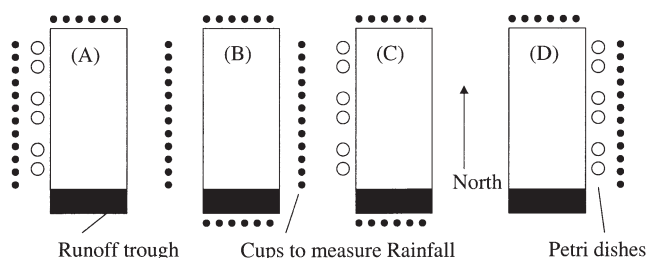

Fig. 2. Lysimeter layout. The four lysimeters are designated Y103A, B, C, and D.

Table 1. Soil properties (from Kelley et al., 1975).

Depth	33 kPa Bulk density	pH	Clay	Silt
m	Mg m^{-3}		%	
0–0.23	1.31	6.0	13.1	78.7
0.23–0.30	1.32	5.0	23.5	71.6
0.30–0.38	1.49	4.8	25.9	69.1
0.38–0.51	1.41	4.8	30.8	63.6
0.51–0.63	1.55	4.7	34.5	57.2
0.63–1.0	1.60	4.5	38.6	51.7
1.0–1.3	1.70	4.5	31.0	52.7

and data logger. More detailed information on lysimeter construction, operation, and recent upgrades can be found in Harrold and Dreibelbis (1951, 1967) and Malone et al. (2000a). Soils, climate, geology, and geomorphology of the area and lysimeters were further described by Kelley et al. (1975).

Lysimeter Experiment

To achieve the objectives, rainfall simulation experiments were conducted in 1999 and 2000 using different herbicides each year with the exception of alachlor application both years (Table 2). Atrazine, alachlor, linuron, and glufosinate were applied on 5 May 1999 before chiseling and corn planting on 12 May and alachlor, metribuzin, and glyphosate were applied on 1 May 2000 before chiseling and soybean planting on 18 May. Herbicides were applied with a tractor-driven sprayer with the boom length long enough to extend over the length of lysimeters in a single pass on the north side of the lysimeters. Herbicide ground deposition rates were measured from 18 Petri dishes placed throughout the lysimeter area in 2000 (Fig. 2) and the deposition rate in 1999 was estimated based on the application efficiency in 2000 (40%) and the target rate. In 2000, half the dishes were analyzed for residual herbicides by rinsing with solvents and half the dishes were analyzed for contact herbicides by rinsing several times with water. Petri dish analysis for both glyphosate and alachlor and metribuzin included rinsing the dish with five aliquots of high performance liquid chromatography (HPLC)-grade water. After the water rinse, dishes analyzed for alachlor and metribuzin included rinsing with 5 mL of ethyl acetate then 5 mL of 50:50 methanol to acetate then 2 mL of ethyl acetate.

Rainfall was initiated less than 2 h after herbicide application and rainfall ceased about 2 h after rainfall initiation (Table 2). Sixty millimeters of rainfall were applied in 1999, and 81 mm were applied in 2000. A large rainfall shortly after herbicide application was simulated to produce a worst-case scenario (Objective 1). Rainfall was produced using an adaptation of the mesoscale rainfall simulator (Sumner et al., 1996) and amount was determined by placing cups around the lysimeters (Fig. 2). The 2-yr, 24-h storm and the 50-yr, 2-h storm

are equivalent to approximately 80 mm of rainfall from the Coshocton, OH, area (Huff and Angel, 1992).

Percolate discrete samples were collected at several times in 1999 and 2000 and composite percolate samples were collected only in 2000 (Table 2). The precise time of collection for the first few discrete samples in 1999 and in 2000 varied by ±0.5 h because the initial flow rate was slow and 100 mL were needed for chemical analysis. In 2000, slot-type rotating composite samplers that collect 2% of the flow were installed on each lysimeter (Malone et al., 2003). Five composite percolate samples were collected between 1 May and 9 May 2000, and about once a week thereafter. The experiment was concluded on 10 May 1999 and on 19 Sept. 2000. The lysimeters were exposed to approximately 490 mm of natural rainfall from 2 May through 19 Sept. 2000.

Herbicide Analysis

Collected alachlor, metribuzin, atrazine, and linuron samples were stored in glass jars near 1°C and unfiltered samples were typically extracted within 3 d using LC-18 solid-phase extraction tubes with 100-mg packing conditioned sequentially with 1 mL ethyl acetate, 1 mL methanol, and 1 mL deionized water. The herbicides were eluted from the extraction tubes with three aliquots of 0.3 mL ethyl acetate. The eluate was concentrated to dryness with nitrogen, then reconstituted with 0.5 mL ethyl acetate and propachlor as an internal standard. Propachlor has never been applied to the lysimeters. Prepared extracts were analyzed using a Model 3500 capillary gas chromatograph equipped with a thermionic-specific detector (Varian, Palo Alto, CA). Each sample was run on two capillary columns of dissimilar polarity (Penton, 1991). When the concentrations differed the lower value was used on the assumption that the higher value was due to positive interference by other compounds.

Glyphosate and glufosinate samples were filtered and frozen until analysis. Glyphosate was quantified using an HPLC and USEPA Method 547 (USEPA, 2003), which involved automated post-column oxidation with hypochlorite and derivatization with o-phthalaldehyde (OPA) and Thiofluor (Pickering Laboratories, Mountain View, CA) followed by fluorescence detection. Glufosinate concentrations were determined by manually derivatizing the sample using the Waters AccTag chemistry package for amino acids, followed by quantification using an HPLC equipped with a Model 600 solvent delivery system, a Model 474 fluorescence detector, and a Model 717 plus autosampler (Waters Corporation, Milford, MA). Minimum detection limits were 0.13 µg L^{-1} (alachlor and linuron), 0.06 µg L^{-1} (metribuzin), 0.03 µg L^{-1} (atrazine), and 5 µg L^{-1} (glyphosate and glufosinate).

Table 2. Selected experimental activities.

Activity	1999	2000
Herbicide application date and time	5 May, 1110 h EST	1 May, 0915 h EST
Applied herbicides and ground deposition rates, kg ha^{-1}†	atrazine (0.89), alachlor (1.4), linuron (0.45), glufosinate (0.16)	alachlor (2.1 ± 1.2)‡, metribuzin (0.11 ± 0.059), glyphosate (0.50 ± 0.23)
Rainfall initiation time	1308 h EST	1000 h EST
Rainfall cessation time	1513 h EST	1202 h EST
Amount of simulated rainfall, mm	60	81
Discrete sample collection time, d after rainfall initiation§	0.13, 0.38, 0.84, 1.1, 1.8, 5.0	0.06, 0.09, 0.10, 0.11, 0.16, 0.22, 0.25, 0.48, 0.86, 1.2
Composite sample collection time, d after rainfall initiation	not collected	−0.05 to 0.22, 0.23 to 0.48, 0.49 to 1.1, 1.1 to 3.2, 3.2 to 7.9, weekly after Day 7.9

† Ground deposition rate in 2000 was measured using petri dishes distributed throughout the lysimeter area (Fig. 2); ground deposition rate in 1999 was estimated based on the measured application efficiency in 2000 (40%) and the 1999 target application.
‡ Average ground deposition rate ± standard deviation.
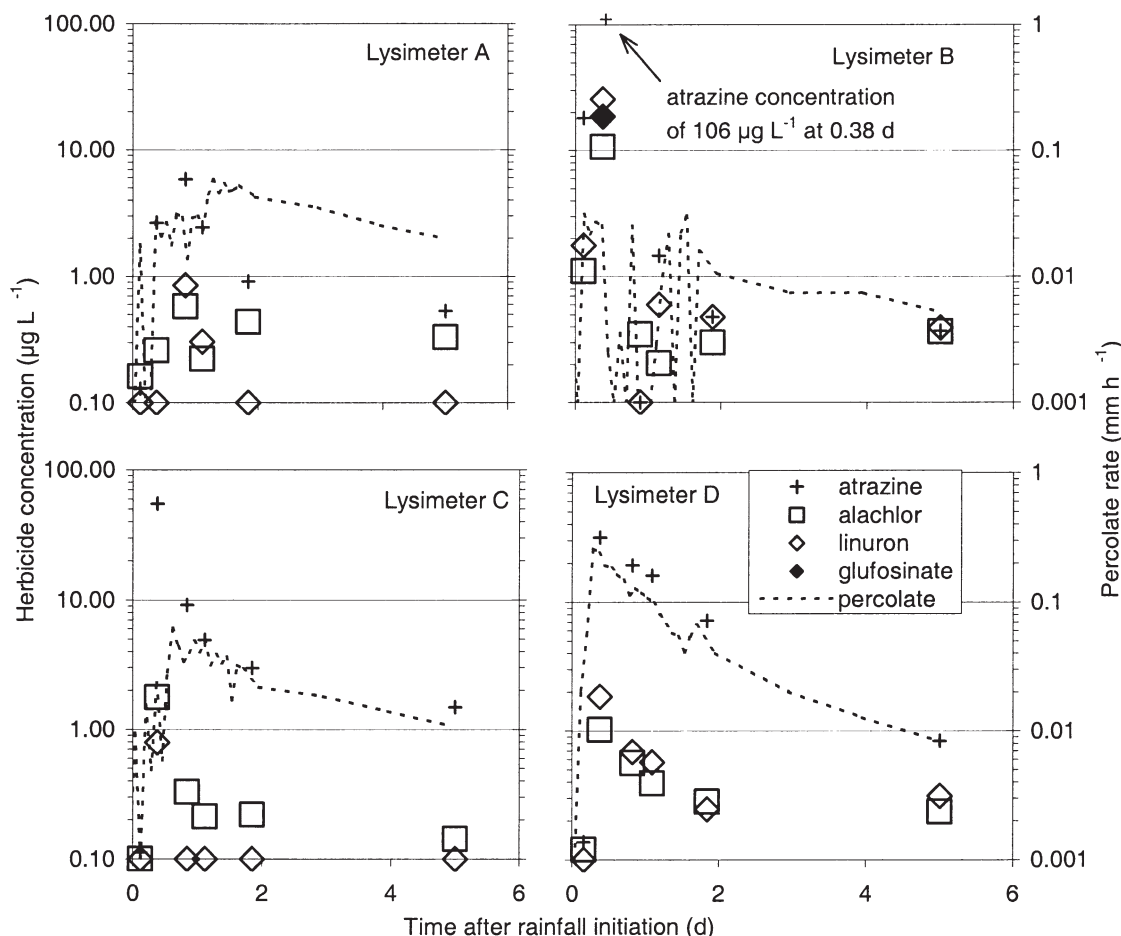§ The precise sampling time for the first few discrete samples after application varied by ±0.5 h.

Fig. 3. The six discrete samples collected after herbicide application in 1999. A concentration of 0.10 µg L^{-1} indicates not detected; a percolation rate of 0.001 mm h^{-1} indicates percolation rate was less than measurable.

RESULTS AND DISCUSSION

Percolate and Herbicide Transport

In 1999 the percolation rates were low and the simulated rainfall amount and rate in 2000 were increased to produce more percolate. The maximum percolation rate in 1999 for Lysimeter D was about 0.3 mm h^{-1} while three of the four lysimeters delivered less than 0.1 mm h^{-1} (Fig. 3). In 2000, the maximum flow rate was greater than 4 mm h^{-1} (Lysimeter B) and the maximum flow rate for the other three lysimeters was greater than 1 mm h^{-1} (Fig. 4). The higher percolation rate in 2000 was partly due to the higher simulated rainfall rate, and higher antecedent soil water content. Percolation amount the day before rainfall simulation was 0.15 mm in 1999 and 0.27 mm in 2000 partly due to rye (*Secale cereale* L.) growing in the spring of 1999 but not in 2000. Another factor that increased percolate after rainfall simulation in 2000 was 23 mm of natural rainfall, which began about 3 h after simulated rainfall ended. The average percolate amount among the four lysimeters in 2000 was 34 mm within 1.1 d after rainfall initiation and 107 mm over the 148-d experiment.

The lysimeter with the highest maximum percolation rate resulted in the highest herbicide transport in 2000. Alachlor transport during the first 1.1 d from Lysimeter B was 0.077% and between 0.018 and 0.023% of applied alachlor from the other three lysimeters. Lysimeter B also had the highest percolation rate while discrete samples from Lysimeter A had the highest metribuzin concentration (15.1 µg L^{-1}) and alachlor concentration (6.5 µg L^{-1}). Herbicide transport amounts are not reported for 1999 because the ground deposition rate is an estimate and the limited number of discrete samples allows only an estimate of flow-weighted concentrations in percolate.

Preferential Flow Characteristics

For the 1999 experiment, it is difficult to draw definite conclusions concerning the arrival time of applied alachlor, atrazine, and linuron because of the high variability among lysimeters and because few discrete samples were collected (Fig. 3). Despite these problems, the peak concentrations coincide for the three residual herbicides (Fig. 3; 0.38 d for Lysimeters B, C, and D and 0.84 d for Lysimeter A). The data also indicate that atrazine losses were substantially higher than alachlor losses (Fig. 3) despite higher estimated alachlor ground deposition (Table 2). The 1999 estimated ground deposition rates should be viewed with caution because flawed Petri dish data collected in 1999 (not reported) suggest that higher linuron
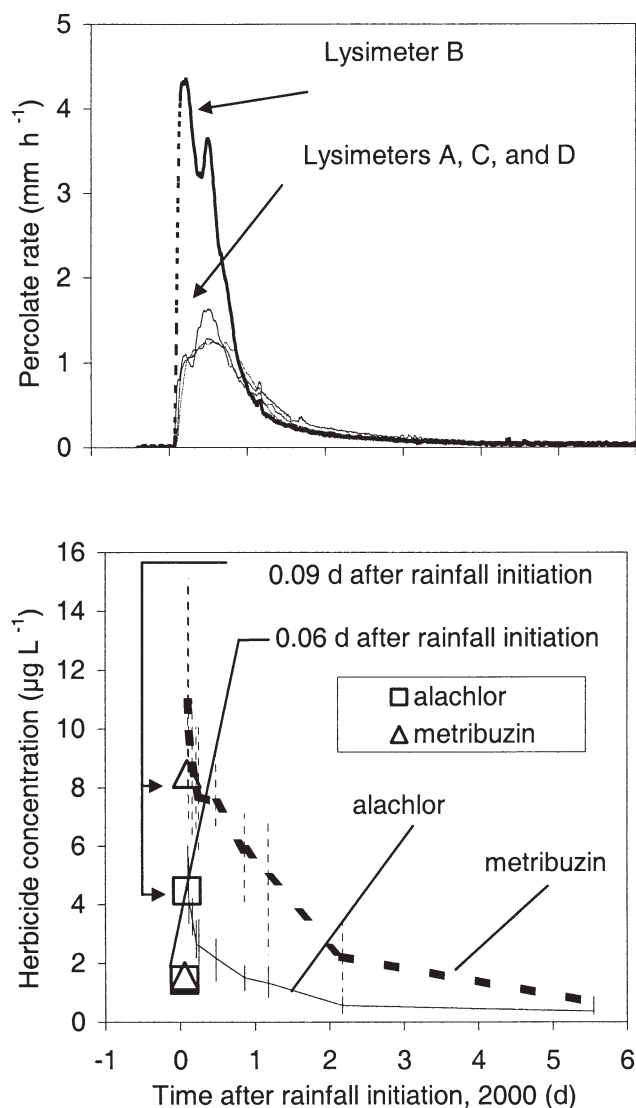
Fig. 4. Chemical concentration in percolate during the first 5.5 d after rainfall initiation (1000 h EST, 1 May 2000). The vertical lines represent the range of concentrations from the four lysimeters. The symbols represent the average alachlor and metribuzin concentration at approximately 0.06 and 0.09 d after rainfall initiation. The maximum concentrations occurred at approximately 0.10 d after rainfall initiation. Herbicide concentration determined from discrete samples except Days 2.2 and 5.5 were composite samples.

Table 3. Residual herbicide transport in percolate at 2.4 m (2000 data only).†

Time	Metribuzin	Alachlor
d after rainfall initiation		
	Percent of applied	
0–1.1	2.21 (1.6)	0.035 (0.028)
0–148	2.58 (1.5)	0.048 (0.029)
	Flow-weighted concentration, $\mu g\ L^{-1}$	
0–1.1	6.65 (1.8)	1.94 (0.59)
1.1–8.0	1.67 (0.77)	0.50 (0.18)
8.0–148	0.29 (0.12)	0.37 (0.15)
0–148	2.51 (0.92)	0.91 (0.34)

† **Results are the average of four lysimeters and the values in parentheses are the standard deviations.**

and atrazine rates may have been applied than estimated from the target application rate (i.e., the 1999 tank mix for atrazine and linuron may have been higher than expected). Jaynes et al. (2001) also observed higher atrazine concentrations than alachlor concentrations in 1.2-m-deep tile drains where irrigation was applied shortly after herbicide application and alachlor and atrazine application rates were similar.

At 0.06 d (1.3 h) after rainfall initiation in 2000, the average concentrations of alachlor and metribuzin were 1.4 and 1.6 $\mu g\ L^{-1}$, respectively, which are above background levels (Fig. 4). The average metribuzin and alachlor background samples taken before herbicide application were less than 0.5 $\mu g\ L^{-1}$. The maximum average concentrations of alachlor (5.0 $\mu g\ L^{-1}$) and metribuzin

(10.9 $\mu g\ L^{-1}$) were detected at 0.1 d after rainfall initiation. A paired t test indicates that the flow-weighted composite concentrations of alachlor and metribuzin were significantly greater within 1.1 d of rainfall initiation compared with composite samples collected between 1.1 and 8.0 d (1.94 vs. 0.50 for alachlor and 6.65 vs. 1.67 $\mu g\ L^{-1}$ for metribuzin, $P < 0.05$; Table 3). The data were split at 1.1 d because the metribuzin and alachlor concentrations were statistically different within 1.1 d (Fig. 5) and most of the pesticide leached within 1.1 d (Table 3).

The coincidence of peak herbicide arrival time at 2.4 m in 1999 and 2000 suggests little difference between the breakthrough times of the herbicides (Fig. 3 and 4), despite the differences in K_{oc} (metribuzin sorption < atrazine sorption < alachlor sorption < linuron sorption; Table 4). The lack of chromatographic separation suggests preferential flow (Flury, 1996). Furthermore, Gamble et al. (1990) predicted a minimum lysimeter water residence time of three months for water applied to a nearby lysimeter with similar construction (Y101D) when assuming water enters the soil surface and moves downward and out of the soil zone as piston flow. The measured soil water content from Lysimeter Y103A on 25 Apr. 2000 was approximately 750 mm and percolate was about 28 mm from 0 to 1.1 d after rainfall initiation; therefore, very little residence water was displaced while the herbicide concentration peaked during this time. In fact, the peak concentration in 2000 occurred at 0.10 d and the flow from rainfall initiation to 0.10 d was 0.4 mm (about 0.05% of residence water displaced). These results are direct field evidence of preferential flow.

Although the breakthrough times were not dependent on K_{oc}, the quantity of transport was K_{oc} dependent. A one-tail paired t test indicates that metribuzin transport was greater than alachlor transport over the first 1.1 d and over the 148-d experiment (2.2 vs. 0.035% for 0 to 1.1 d, $P < 0.05$; Table 3). Furthermore, significantly higher metribuzin concentrations were collected than for alachlor from 0.10 through 1.2 d (Fig. 5), despite an alachlor ground deposition rate about 20 times higher (Table 2). Glyphosate was not detected in percolate at concentrations above the 5 $\mu g\ L^{-1}$ detection limit throughout the experiment, which was expected given the glyphosate application rate (0.5 kg ha^{-1}) and its approximate partition coefficient (23 150 mL g^{-1}).
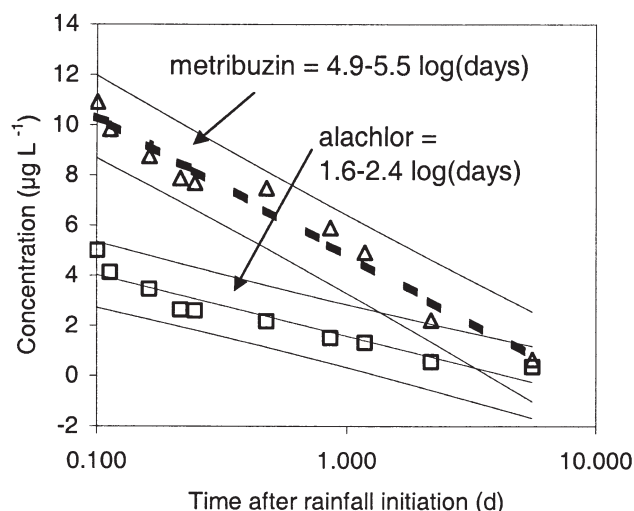
The metribuzin and alachlor percolate concentrations

Fig. 5. Logarithmic presentation of 2000 average concentration with 95% confidence intervals. Note that log(1) = 0, therefore the *y* intercept is at 1.00 d after rainfall initiation. Time zero is 1000 h EST, 1 May 2000 (rainfall initiation). The symbols represent the average alachlor and metribuzin concentration from the four lysimeters.

decreased significantly with time ($P < 0.0001$) as indicated by negative slopes (Fig. 5). Shipitalo and Edwards (1996) observed a similar phenomenon while investigating the fate of alachlor and atrazine during the first rainfall after application using 30-cm-deep undisturbed blocks brought into the lab. Shipitalo and Edwards (1996) suggested that more surface-applied chemicals may move into the soil matrix with increasing rainfall where they are less susceptible to leaching via preferential flow. Rapid herbicide concentration decrease with time has also been observed in runoff studies (e.g., Edwards et al., 1997). The quasi-exponential pesticide concentration decrease with time during rainfall has been observed in runoff studies, apparently because more pesticide leaches into soil matrix and becomes less available for runoff (Wauchope et al., 1990).

Residual and Contact Herbicide Transport

Out of six discrete samples collected for each of the four lysimeters in 1999 (24 total discrete samples), glufosinate was detected in only one sample (Lysimeter B, 19 μg L^{-1}; Fig. 3). Atrazine concentration, however, was greater than the MCL (3.0 μg L^{-1}) for 10 of 24 samples (Fig. 3). Alachlor concentration was above its 2.0 μg L^{-1} MCL only for the 0.38-d sample from Lysimeter B (11 μg L^{-1}). The highest measured atrazine concentration (106 μg L^{-1}) was also from Lysimeter B at 0.38 d. Although glufosinate was detected in only one sample, it is likely a real detection because it coincides with the peak concentration of the three residual herbicides (Fig. 3). Although an MCL of glufosinate has not been established, Wauchope et al. (2002) reported that glufosinate would have an MCL of 150 μg L^{-1} using the same standard procedures for calculating the glyphosate MCL (700 μg L^{-1}).

In 2000, the majority of alachlor and metribuzin was transported in percolate during the first 1.1 d after rainfall initiation (Table 3). During this period, the average flow-weighted alachlor concentration was 1.94 μg L^{-1} (Table 3), which is similar to its MCL of 2 μg L^{-1}. The average flow-weighted metribuzin concentration was 6.65 μg L^{-1} (Table 3), which is less than its Lifetime Health Advisory level by a factor of 30 (metribuzin LHA = 200 μg L^{-1}; USEPA, 1988). Glyphosate was not detected throughout the experiment (minimum detection limit = 5 μg L^{-1}). Therefore, the average glyphosate concentration was less than its MCL (700 μg L^{-1}) by at least a factor of 140.

CONCLUSIONS

The contact herbicides glyphosate and glufosinate have higher MCLs, which are determined partly based on human health, and higher sorption to soil (K_{oc}) than traditional soybean and corn residual herbicides such as alachlor and atrazine. The MCLs for glyphosate, glufosinate, alachlor, and atrazine are 700, 150 (estimated), 2.0, and 3.0 μg L^{-1} and the approximate K_{oc} values are 23 000, 400, 160, and 120 mL g^{-1}, respectively. This suggests that glyphosate and glufosinate should leach at levels of less concern than alachlor and atrazine, but under conditions of preferential flow the risk is uncertain.

In this study, most of the herbicide leaching to 2.4 m was dominated by preferential flow. For example, the peak herbicide concentration in 2000 was reached at 0.10 d after rainfall initiation but the measured percolate during this time was only about 0.05% of residence soil water. Also, the peak concentrations of herbicides with different sorption to soil coincided both years. That is, atrazine, alachlor, and linuron (linuron $K_{oc} \geq 400$ mL g^{-1}) concentrations peaked at the same time in 1999, and alachlor and metribuzin concentrations peaked at the same time in 2000. Although chromatographic separation between herbicides was not evident, metribuzin had higher percolate concentrations than the more strongly sorbed alachlor within the first 1.2 d after rain-

Table 4. Herbicide partition coefficients normalized for soil organic carbon (K_{oc}) from several sources.

	Residual				Contact	
Source	Atrazine	Alachlor	Linuron	Metribuzin	Glufosinate	Glyphosate
				mL g^{-1}		
USDA (2004)	147	124	496	52	430	2 100
Wauchope et al. (2002)	156	170	NR†	NR	600	22 300
Kladivko et al. (1991)	91	157	NR	NR	NR	NR
RZWQM pesticide properties database‡	100	170	400	60	100	24 000
Malone et al. (2001)	105	195	NR	NR	NR	NR

† Not reported.
‡ From the Root Zone Water Quality Model (RZWQM) default input.

fall initiation in 2000 despite an alachlor ground deposition rate about 20 times greater.

Percolate concentrations of glyphosate and glufosinate did not approach the MCL. Glyphosate was not detected and only one 19 $\mu g\ L^{-1}$ sample of glufosinate was detected. The minimum detection limits of glyphosate and glufosinate were 5 $\mu g\ L^{-1}$, but these high detection limits relative to alachlor and atrazine detection limits were acceptable because of the relatively high glyphosate and glufosinate MCLs. In 1999, 10 of 24 atrazine samples were above the MCL and in 2000 the flow-weighted alachlor concentration within the first 1.1 d after rainfall initiation was 1.94 $\mu g\ L^{-1}$.

These results confirm other studies indicating that pesticide transport mass below the root zone is dependent on herbicide sorption, but travel time is independent of sorption when macropore flow occurs (Kladivko et al., 1991; Flury et al., 1995; Elliott et al., 2000; Jaynes et al., 2001). Even though rapid herbicide transport occurred through preferential flow to a depth of 2.4 m, glyphosate and glufosinate were not observed to approach concentrations of environmental concern because of the high MCLs and the relatively strong sorption to soil.

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